

^{17}O -NMR Knight shift study of the interplay between superconductivity and pseudogap in $(\text{Ca}_x\text{La}_{1-x})(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y$

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We report systematic ^{17}O -NMR measurements on the high- T_C cuprate $(\text{Ca}_x\text{La}_{1-x})(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y$, for four different families (different x). Using Knight shift data, we show that the pseudogap lines for all families are inconsistent with a quantum critical point inside the superconducting dome. In addition, at constant doping the pseudogap temperature does not vary with x , in contrast to T_C . We therefore argue that pseudogap and superconductivity are separate phenomena in these cuprates.

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The pseudogap (PG) is still one of the most important and yet among the least understood features of cuprate physics [1–5]. It is experimentally seen as a partial gapping of the electronic spectrum below an onset temperature T^* , mostly in the underdoped part of the cuprate phase diagram. Although such a gapped area of the phase diagram has been found in all hole-doped high- T_C superconductors so far, the universality of its characteristics is controversial. In the underdoped region, the pseudogap onset temperature T^* decreases as hole doping increases, but in the optimally doped and overdoped regions the behaviour (and indeed the existence) of the pseudogap is uncertain. It has been argued that the PG line intersects the superconducting (SC) dome in the phase diagram – as seems to be the case in the best studied cuprate, $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) – or merges with the dome on the overdoped side [6]. Although it has long been speculated that the pseudogap is in some way related to high- T_C superconductivity, these conflicting possibilities preclude any general agreement on the nature of such a relation. The pseudogap state could be a direct precursor to superconductivity, coexist independently, or compete [2, 7–9]. It is even ambiguous whether T^* is a true phase transition [10] or simply a crossover temperature.

An idea which has recently attracted increased attention due to results on YBCO is a connection between superconductivity, pseudogap and quantum critical behaviour [11]. In that picture the pseudogap line is a line of real phase transitions, intersecting the superconducting dome close to optimal doping and ending in a quantum critical point (QCP) at $T = 0$. A loop current model has been proposed in this context to explain the phase diagram [12], while several experiments indicate the existence of circular currents in underdoped YBCO [13, 14], and recently evidence was found that a thermodynamic phase transition indeed occurs at (or close to) T^* [10]. This brings up the important question whether such a model for the pseudogap is universal

in all cuprates, and, more generally, if high- T_C superconductivity as such is a consequence of quantum criticality? Due to several advantages – relative structural homogeneity, high transition temperatures, and quality of available crystals – YBCO is the most studied cuprate [15, 16] (at least in terms of pseudogap physics) and there is a tendency to regard results on YBCO as universal. It is our purpose to discuss pseudogap data for a structurally very similar system of cuprates – $(\text{Ca}_x\text{La}_{1-x})(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y$ (CLBLCO), in order to check PG universality in cuprates. We show strong experimental evidence that the quantum critical behaviour of the pseudogap line is not universal, as T^* is still very far from SC dome in optimally doped CLBLCO, in spite of very similar critical temperatures and structural features compared to YBCO. Our data instead support the notion that pseudogap and superconductivity are coexisting phenomena, with no simple relation between them.

$(\text{Ca}_x\text{La}_{1-x})(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y$ is a unique system in which one may chemically control not only the oxygen doping y , but also the maximum T_C for the optimal oxygen doping (by changing x). It has an YBCO-like structure for all families (x) and oxygen doping levels (y) [17] (see Fig. 1). All samples are tetragonal and there is no chain ordering. CLBLCO families have negligible structural differences [18], but the highest superconducting transition temperature varies up to 30% between families [19]. T_C is around 80 K for optimally doped ($y \approx 7.15$) sample from the $x = 0.4$ family – close to optimally doped YBCO. As can be inferred from NMR measurements on Cu and Ca nuclei [20, 21] and confirmed by ^{17}O NMR in this work, the level of disorder in CLBLCO is family independent and similar to the 214 family of cuprates ($\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ – LBCO, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ – LSCO). This is not unexpected, since the level of ionic substitution is similar to LBCO. On the other hand, by increasing x the maximum

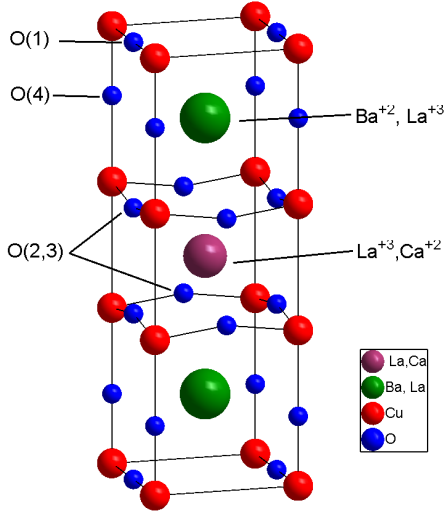


Figure 1. (Color online) CLBLCO unit cell, which is very similar to YBCO cuprate. There is no ordering of chain oxygen O(1). Notice the buckling angle of planar oxygen O(2,3). Angle is controlled by changing the Ca to La ratio on the YBCO Y site (by x), and compensating by the Ba to La ratio on the YBCO Ba site, in a manner that leaves the valence constant.

critical temperature also increases, displaying a considerable insensitivity to out-of-plane ionic disorder. One can roughly imagine the CLBLCO families to be an extension of YBCO, with the advantageous possibility of systematically tuning electronic interactions by changing the family x without drastic changes in crystal structure. Another advantage is that CLBLCO can be highly overdoped by increasing oxygen concentration y . Hence, the superconducting dome is well defined on the overdoped side, in contrast to YBCO. Similar structures with varying superconducting and magnetic properties thus make CLBLCO ideal for understanding the relation between superconductivity and pseudogap temperature.

We present ^{17}O nuclear magnetic resonance (NMR) results for four different CLBLCO families ($x = 0.1 - 0.4$). The $x = 0.1$ family was comprehensively studied by measuring six samples with different oxygen doping, while the other families ($x = 0.2 - 0.4$) were represented by two or three different dopings. Before the NMR measurements, all samples were characterised with a SQUID magnetometer and all show single-component superconducting transition. The CLBLCO samples were in powder form, enriched with the NMR active oxygen-17 isotope with spin $I = 5/2$. Only underdoped and nearly optimally doped samples have been measured because of technical difficulties in enriching the overdoped samples with ^{17}O . Nevertheless, the underdoped samples also give valuable insight into pseudogap behaviour in the phase diagram.

NMR spectra were acquired with a Tecmag Apollo spectrometer, in an Oxford superconducting variable-

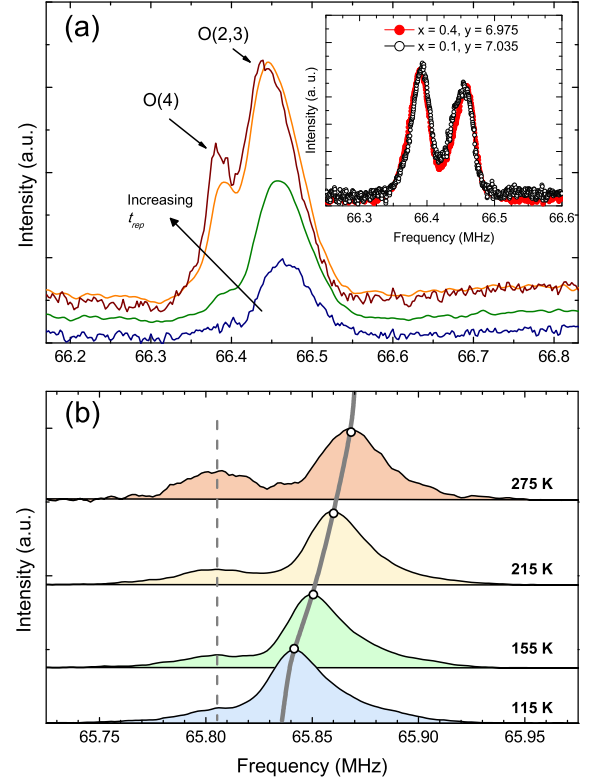


Figure 2. (Color online) (a) Central NMR transition of ^{17}O with two distinct lines recorded with repetition times (t_{rep}) of 3 (black), 10, 150 and 300 ms (red). The apical oxygen site O(4) has much slower spin-lattice relaxation than in-plane oxygen O(2,3). Sample: $x = 0.4$, $y = 7.1$. Inset: comparison of two different families ($x = 0.1$ and 0.4) at (approximately) same oxygen doping y . The difference between linewidths are 6% for apical and negligible for in-plane oxygen. (b) Spectra at different temperatures. Thick grey line follows in-plane oxygen peaks. The shift of the apical oxygen is temperature-independent, as is denoted by dashed line. Intensity of apical oxygen is not the same because its relaxation time shortens with temperature. Sample: $x = 0.1$, $y = 7.05$.

field magnet at different magnetic fields in the vicinity of 11.5 T. Spectra were acquired by a standard Hahn echo sequence, followed by Fourier transform of the echo signal. The only previous ^{17}O NMR study on CLBLCO [22] was concerned with the nuclear quadrupole resonance parameter ν_Q – here we focus on the central transition ($-1/2 \leftrightarrow 1/2$) where we found two distinct NMR lines from different oxygen sites.

In Fig. 2a we show spectrum for different repetition times (t_{rep}) between NMR data acquisitions. For slow nuclear spin-lattice relaxations ($t_{\text{rep}} < 5T_1$) nuclei cannot return to equilibrium in time for another acquisition. This results in signal reduction [23]. By increasing repetition time we get saturation for higher frequency line at $t_{\text{rep}} > 150$ ms, while lower frequency line remains unsaturated, implying slower spin-lattice relaxation. This

is expected for cuprate superconductors [24, 25]. Based on YBCO results, we assign the line at lower frequency (slowly relaxing) to apical oxygen O(4), while the fast-relaxing line at higher frequency comes from the in-plane oxygen O(2,3). The third oxygen site O(1) which would correspond to the chain oxygen in YBCO, is difficult to see in powder samples due to disorder-induced broadening (far from planes), and we do not observe it.

The ^{17}O -lines are similar in width in all measured samples, leading us to conclude that structural disorder is constant through all families (as seen by NMR). Comparison of disorder in different families can be seen in inset of Fig. 2. Gaussian fits to spectra give negligible linewidth difference for planar oxygen. In contrast, apical oxygen in $x = 0.4$ sample has 6% wider line than $x = 0.1$. This confirms that disorder is small and far from CuO_2 planes. It is thus safe to say that any differing behaviour is purely due to electronic properties.

The in-plane oxygen shows a temperature-dependent Knight shift, while the apical site has no visible shift (Fig. 2b), also in agreement with other 123-cuprates [26]. Using measured values of the Knight shift, one can determine the in-plane spin susceptibility at the oxygen site, $\chi_s(T)$, from

$$K(T) = K_{orb} + a\chi_s(T), \quad (1)$$

where K_{orb} is orbital shift due to bound electrons and a is hyperfine coupling. By lowering the temperature, we observe a reduction in spin susceptibility, which is a characteristic signature of the opening of a spin gap [26, 27]. In order to determine the pseudogap characteristic temperature T^* from the temperature dependence of the Knight shift, we have employed an often-used phenomenological three-parameter function [28]:

$$K(T) = \frac{\chi_0}{\cosh^2(T^*/2T)} + K_{orb}. \quad (2)$$

As can be seen from Fig. 3, the fit is very good above T_c .

In inset of Fig. 4 we show our Knight shift results for the $x = 0.1$ and $x = 0.4$ families and compare them with previous CLBLCO T^* data on the same family obtained by SQUID magnetization [29] and Ca-NMR Knight shift measurements [21]. As can be seen, the study justifies earlier analysis, with the largest discrepancies arising from SQUID $x = 0.1$ data. Since NMR directly probes local spin susceptibility on oxygen sites *in the planes*, and the oxygen Knight shift being sensitive only to pseudogap opening (with no large additional signal, as in SQUID measurements), we concur that our ^{17}O -NMR measurements are the most reliable of the three experimental methods. The general behaviour of the pseudogap onset temperature agrees with other cuprates: T^* is higher for more underdoped samples, and decreases seemingly linearly with increased oxygen content (y). However, the

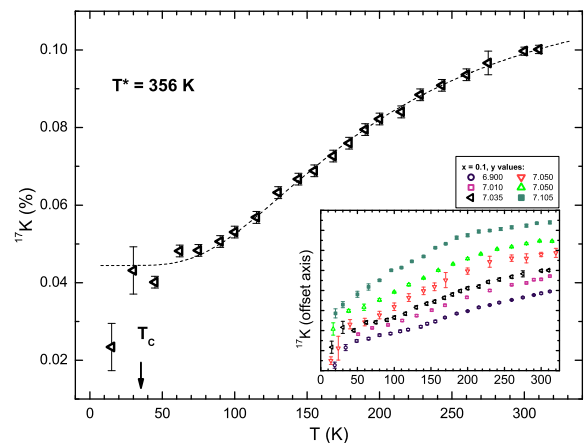


Figure 3. (Color online) In-plane oxygen line position in reference to apical oxygen position for sample $x = 0.1$, $y = 7.035$. For fitting, only points above the superconducting transition T_c are taken into account. As the gap opening is not abrupt, the pseudogap temperature T^* is not easily distinguished in the plots, but acquired as parameter from a fit function (dotted line - see text). Inset: Knight shifts for $x = 0.1$ samples with various y all show similar behaviour. Each sample is offset on vertical axis for better display.

nearly optimally doped samples still show a strong temperature dependence of the spin susceptibility. Unless there is some abrupt change in the pseudogap line (e.g. steepening into the superconducting dome or levelling off to a constant value), it appears that the pseudogap only merges with superconductivity on the highly overdoped side (as can be seen from $x = 0.4$ sample), or doesn't merge at all ($x = 0.1$ sample). This result implies different PG behaviour with respect to SC dome in various families. It is also inconsistent with theories that predict QCP near optimal doping.

A more uniform picture emerges if we allow for the fact that the oxygen doping y is not a good measure of mobile holes in the planes. As discussed earlier [20, 29–31], μSR and NQR measurements indicate that the proper doping parameter for CLBLCO is Δp , the difference of in-plane hole doping, p , from optimal doping p_{opt} for the given family. Δp is related to chemical oxygen doping y via

$$\Delta p = K(x)(y - y_{opt}),$$

where y_{opt} is the chemical doping of optimal sample and $K(x)$ is a family-dependent parameter that accounts for plane doping efficiency [20]. If Δp is used in place of y , all SC domes acquire a similar shape (with a slight discrepancy on the overdoped side). In Fig. 4 we show the scaled phase diagram with results from all families. Although the lack of samples with wide y variation in $x = 0.2 - 0.3$ prevents us from making any strong assertions there, it can still be seen that all the data is consistent: spectral widths, frequency and temperature

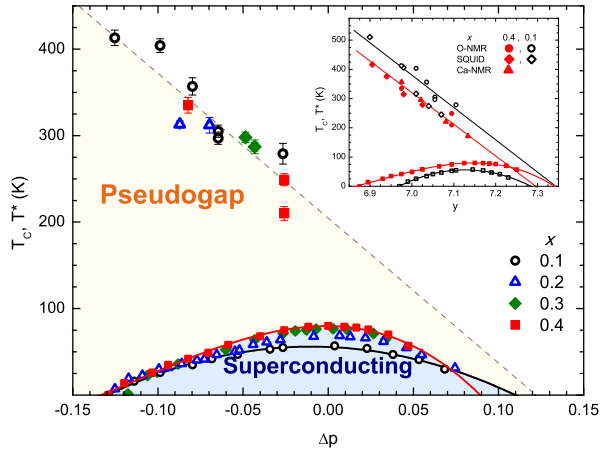


Figure 4. (Color online) CLBLCO phase diagram for all measured samples. Chemical doping y is replaced with the in-plane hole concentration relative to optimal doping, Δp . The dashed pseudogap line was obtained from a linear fit to all T^* points shown. The pseudogap line falls to zero at $\Delta p = 0.12 \pm 0.02$. Inset: Comparison between O-NMR measurements presented in this paper and Ca-NMR and SQUID susceptibility measurements from [21, 29]. Presented are only $x = 0.1$ and $x = 0.4$ samples. Abscissa is oxygen doping parameter y .

behaviour differ only slightly between families. All T^* points collapse roughly onto the same line, falling to zero at $\Delta p = 0.12 \pm 0.02$ (as determined by linear regression), far from the superconducting dome.

From the unscaled raw data it is apparent that the family with highest T_c tends to have the lowest T^* , and vice versa. Once the ‘true’ hole doping is introduced, the anticorrelation is less pronounced, but it remains certain that T^* is much less affected by a change in x than the superconducting transition temperature. Such a weak correlation between pseudogap and superconductivity shows that the position of the quantum critical point (if it exists) is not universally close to optimum doping, but depends on the details of the system, leading us to conclude that the high-temperature superconductivity is not a quantum-critical fluctuation effect. The data instead suggest that superconductivity and pseudogap are separate phenomena, with no simple relation between them.

As for the nature of the pseudogapped state itself, the near-constancy of T^* with changing x places constraints on any theory of the pseudogap. If the pseudogap is due to a distinct ordering (such as incommensurate spin density wave, orbital density wave, or similar), the order must be insensitive to the lattice deformations (and corresponding variation of electronic hopping integrals) brought upon by changing x [20, 31]. A weak correlation between the Néel temperatures of underdoped CLBLCO and T^* was observed in a magnetic susceptibility study, indicating a magnetic origin of the pseudogap [29]. The

intrinsic uncertainty of T^* , the small variation of T_{Neel} between families and the relatively small number of differently doped samples investigated prevent us from giving definite conclusions about the scaling of T^* with T_{Neel} in this study. However, as mentioned above, we do observe that the relative variation of T^* with x is much smaller than the change in T_c (noting that the influence of x on T_c is an interesting subject itself [22]). In view of the relative robustness of T^* , the prospect of pseudogap as a generic consequence of Mott physics seems appealing to us [32], but detailed calculations and more extensive experiments are needed in order to substantiate the proposition.

To conclude, we have detected a spin gap in the Knight shift of in-plane oxygen atoms in the cuprate family CLBLCO, confirming the universality of the pseudogap in cuprates and gaining new insight into the nature of the pseudogap state. Our systematic ^{17}O investigation of CLBLCO families shows that the local level of chemical disorder is similar in all investigated samples, making them suitable for investigating purely electronic effects. We observe differences in the behaviour of pseudogap and superconductivity among different CLBLCO families, with the pseudogap line extending far into the overdoped side of the phase diagram. This is strong evidence that high- T_c superconductivity is generically *not* a quantum critical phenomenon, but instead suggests that pseudogap and superconductivity are separate phenomena. As the in-plane electronic parameters vary smoothly across all investigated CLBLCO families, the differing behaviour of superconductivity and pseudogap is here visible with unprecedented clarity, providing an important benchmark for theories of the pseudogap state.

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